

Environmental Remediation Sciences Program
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Summary of Breakout Session on
Coupled Physical, Chemical and Biological Processes

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The following is a summary of the discussions that took place during the breakout session on coupling between physical, chemical and biological processes in subsurface environments, and how process coupling impacts the development of models that can accurately predict the transport and transformation of contaminants of concern at DOE facilities.

Session Abstract

The fate and transport of contaminants in the environment is a result of biological, chemical and physical processes. Predicting the fate of contaminants depends not only on accounting for the actions of independent single component process, but also on how the processes are coupled. The degree to which process coupling controls the state and distribution of contaminants remains largely unresolved making it difficult to develop practical conceptual models, which therefore leads to uncertainty in quantitative predictions. A great deal of progress has been made in understanding details of individual physical, chemical and biological processes that shape the behavior of complex, heterogeneous subsurface environments. Much of this work, and complementary field studies, has been supported by the EMSP and NABIR programs. An important next step will be to understand how system behavior depends on individual processes that are coupled together, particularly at the field scale. Practical models for whole-system behavior are still elusive, particularly models that can predict how systems respond to natural or engineered events which occur over different temporal and spatial scales. Are there key advances that would help researchers significantly accelerate progress, experimentally or computationally? How can the emerging capabilities in genomics, proteomics and metabolomics be used to understand the nature of subsurface systems and how do they respond to natural or engineered impacts? Are there biogeochemical tools or approaches that can be applied to help translate coupled processes from molecular to field-scales? What is the role of modeling in analyzing the coupled system behavior? Can knowledge of small-scale processes measured in isolation be scaled to describe system behavior? How do we deal with the non-linear behavior of increasing process complexity in going from isolated laboratory to field studies? And, perhaps most importantly, what evidence do we currently have that suggests that process coupling must be accounted for in order to accurately simulate system behavior or does process coupling represent unnecessary model complexity?

The ERSP will be working to outline new frontiers that provide groundbreaking information on describing the fate and transport of contaminants within the subsurface

and in helping to design remediation efforts were feasible. The foci of this breakout session are two-fold: (i) to define key questions currently limiting our understanding, and thus prediction, of coupled processes (physical, chemical, and biological), and (ii) developing means to overcome these limitations for both prediction and remediation efforts. Examples from current EMSP/NABIR projects are highlighted.

Session Organization:

The breakout session was organized around three primary questions (provided below). Research related to the questions was illustrated by presentations from ERSD researchers and discussion periods. The session was concluded with a summary of primary challenges the participants felt should be priorities of future research.

Question 1a: What type of experiments can help reveal and quantify physical, chemical and biological process coupling?

Presentation briefs:

- **Jon Lloyd, University of Manchester:** *Techniques useful for dissecting microbially mediated processes, including sediment incubations, reactive columns, and progressive microcosms.* Dr. Lloyd discussed the use of current molecular biological and geochemical tools for examining biogeochemical processes. Improvements in cell physiology, method sensitivity, analytical resolution, facilities for working with radioactive systems, and extrapolation to field scales were indicated as needing more attention in the future.
- **Colleen Hansel, Stanford University:** *The need to first define the diversity of organisms at a site and then determine the operating metabolic processes.* Dr. Hansel showed how identification of metabolic intermediates can help improve our understanding of the overall kinetics of contaminant degradation or transformation by showing where other processes can affect, intercept, or inhibit the reactions of intermediates and therefore must be incorporated into predictive models. Such research leads not only to an understanding of metabolic rates in natural systems, but also to approaches to controlling the rates and the distribution of metabolic products.
- **Jaimin Wan, Lawrence Berkeley National Laboratory:** *The need to (1) quantify known processes and (2) identify unknown processes.* We need to understand how physical and biogeochemical processes can impact the properties of porous media at permeability boundaries that subsequently impact: 1) where biogeochemical processes take place, 2) the rates of mass transport across boundaries, and 3) how to understand averaged macroscopic system behavior. It is also necessary to quantify known processes in appropriate terms (e.g., not as effective parameters) in order to show where it is necessary to search for unknown processes or understand process coupling in order to improve the accuracy of model predictions. Further research efforts should be directed at long-term experiments and experiments that are designed with field conditions in mind yet are simple enough to resolve and quantify individual reaction mechanisms.

Question 1b: How do we approach deciphering coupled processes at the field-scale?

Presenters:

- **Phil Long, Pacific Northwest National Laboratory:** *A summary of uranium reduction at the Old Rifle site resulting from established biogeochemical*

gradients. Physical and biogeochemical measurements and modeling were described, as well as the interdependence between physical and biogeochemical processes. The overall system dynamics, in which the various reaction pathways (dissimilatory Fe reduction and sulfate reduction) are distributed in space rather than purely in time, are not clear at this stage. For example, bioavailable Fe(III) phases are depleted near the well bore, thus reducing the activity of Fe reducers that are responsible for most of the U(VI) reduction. This allows for a transition to sulfate reduction. Fe(III) reduction, therefore, shifts downstream to where bioavailable Fe(III) phases are still available, however this zone is now impacted by a flux of H₂S that can react with, and reduce, Fe(III) phases directly. This is a prime example where the reaction network needs to be coupled to transport, both in conceptual and numerical models.

- **Craig Criddle, Stanford University:** *A review of a biostimulated uranium reduction at the Oak Ridge Field Research Center illustrating coupled relationships between amendment delivery, gas production and utilization of amendments.* A field project lead by Dr. Criddle has established forced gradients at the research site to reduce and immobilize uranium as insoluble U(IV)-oxide. Although several of the individual biological and chemical processes are well studied, and the principles being applied are appropriate, the inducing the desired outcome under field conditions is challenging, and includes the competition between multiple processes that affect flow (via gas formation) and the dominant chemical transformations. Dr. Criddle emphasized the need for comprehensive geophysical, chemical, biological, and hydrologic measurements that are needed to develop good interpretations of system behavior.

Question 2: What conceptual and numerical modeling approaches are needed to capture process coupling at the laboratory and field scale? What information is needed for the models? What is or is not useful input for computational models?

Presenters:

- **Carl Steefel, Lawrence Berkeley National Laboratory:** It was argued that most reactions of biogeochemical interest occur in open systems where the flux(es) of reactive species drives reactions. Therefore, a reactive transport approach is generally required. Of key interest here is to compare the time scales of biogeochemical processes to those of transport, since this will govern the extent of reaction over a particular spatial domain, as in the example of U(VI) reduction at the Rifle site. Finally, it was argued that it is essential to begin rather than end, with mechanistic models since probability-based performance assessment models discard many if not most of the scientific considerations at an early stage. The greatest challenge in implementing coupled models, whether conceptual or numerical, is training a new generation of geoscientists in **both** dynamic system analysis and in the basic biogeochemical, hydrologic, and microbial processes. Unfortunately, progress in this arena is difficult to detect as most geoscience departments gradually migrate towards increasingly specialized research personnel.
- **Peter Lichtner, Los Alamos National Laboratory:** Full scaling between the pore scale and the field scale is still not possible, but Lattice-Boltzmann methods can be used to develop quantitative reactive transport models at the pore-scale. Such models are much closer to capturing the actual mechanisms by which subsurface processes take place and they may be useful even at this early stage in investigating pore-scale effects (e.g., clogging of individual pores by

precipitation) and their effect on bulk properties like permeability. The usefulness of such computational studies will be limited by the lack of direct experimental kinetic and transport measurements at the pore-scale, although the new generation of microscopic and spectroscopic techniques, especially at the DOE synchrotron facilities, offer hope that progress can be made here.

Question 3: What is the evidence that process coupling needs to be addressed? How do we link laboratory experiments to field-scale processes? What degree of system characterization (information) is needed, and how is this different from systems where process coupling is not important?

Opinions expressed by discussants:

John Zachara, Pacific Northwest National Laboratory: It is important to consider parameters of specific environments and whether natural or perturbed conditions prevail. Detailed lab studies are essential for solidifying process coupling, but it must be recognized that scaling from lab to field environments is still difficult.

Scott Brooks, Pacific Northwest National Laboratory: Need to continually scrutinize micro-scale measurements for their relevance and applicability in modeling field-scale systems.

Eric Roden, Pacific Northwest National Laboratory: Need to emphasize how microbial communities change and respond to perturbations at the field-scale and track changes over short time periods (days).

Summary of Points made in the breakout session:

- **Definitions of process coupling vary.** There are different perceptions about what it means for processes to be coupled. In many cases, processes are coupled linearly in the sense that each can be quantified independently of the others, and then assembled to describe system behavior. With respect to biological and geochemical processes, it is possible to describe system behavior with ever-increasing resolution in the number of processes.

Example 1: $Y = f_1(x_1) + f_2(x_2) + f_3(x_3)g(x_4) \dots$ where response Y is a function of processes f_i and g_i that are dependent on parameters x_i

An example is modeling reactive transport where hydrological or diffusion processes control physical migration of solutes, while sorption on mineral surfaces is modeled with a partitioning function. Each process can be studied independently with retardation of solutes being predicted by a simple combination of the processes. However, observations from such a system must be interpreted by combining the various processes, as in the Rifle U(VI) bioremediation site described above where discrete reaction zones are distributed in space rather than purely in time.

In contrast, process coupling can include an explicit feedback loop that is more complicated and results in non-linear, and sometimes unstable, behavior. The interdependence needs to be appreciated in scaling from simple to complex (field scale) systems and in modeling.

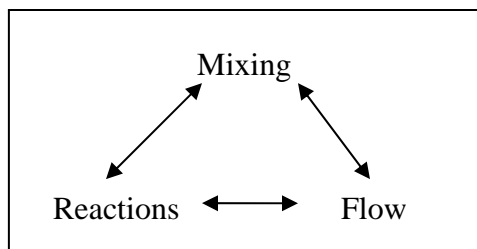
Example 2: $Y = f_1(f_2(Y), x_1)$: Where a product, or outcome, is the result of one or more component processes that are functions of the product or outcome.

An example is how a precipitation event, or biofilm formation, can modify fluid flow rates and flow paths. Since the processes that lead to modification of flow are dependent on the delivery of reactive solutes, the type of dependence between processes is more complex.

Some commentators have argued that coupling refers only to this nonlinear feedback between reactions and flow, but a much broader definition is provided by any case where one process affects the other (e.g., transport and biogeochemical kinetics). Again, the important point is that even in the case where the various processes are largely additive, interpretation of field and even laboratory observations needs to be within this overall dynamic framework.

- **Needs, applications and research challenges for the future (a summary of points and statements made by session participants):**

- Goals must be to interpret the evolution of system properties (e.g., heterogeneity, rates, partitioning), not just describe system-specific behavior.
- The nature of process coupling will depend on physical and temporal scales.
- Illustrating the significance of process coupling in systems that are perturbed at different rates is important particularly for engineered systems where changes are rapid.
- Links should be made between transient fluxes through preferential flow paths and long-term speciation/stability of inorganic contaminants.
- Lab and field studies of coupled processes must be better integrated, and it will be important to iterate between them. (Iteration can be difficult to achieve with traditional funding mechanisms.)
- Understanding the vadose zone / saturated zone interface: microbial, geochemical and hydrologic processes is of particular importance because of the nature of processes that depend on (are coupled to) mass transport
- Must solve challenges related to the delivery and *in situ* mixing of amendments
- The relationships between fluid mixing, reaction rates precipitation/dissolution, biofilm growth/decay, etc. need to be investigated.
- ...
- There is a practical need to accelerate processes that are already naturally occurring with predictable outcomes.
- Need to interpret changes in permeability and flow, for example, in permeable reactive barriers and caps.
- Model predictions must improve and should be able to distinguish between short-term and long-term system behavior and properties.
- Determining the importance of geochemical-hydrological processes (independent of biology) is also critical.
- Microscopic reactions and transport controlling long term release rates will be important for environmental stewardship.



Recommendations: Within natural environments (surface and subsurface), processes controlling the fate and transport of contaminants seldom occur in isolation, but rather are typically the result

of coupling between biological, chemical, and physical factors. Nevertheless, isolated processes remain the dominant focus for research, both experimentally and computationally, because it is still intuitively important to understand individual component processes, but also owing to the difficulty in representing and quantifying coupled processes in experiments and models. In addition, a thorough understanding of individual processes is essential if mechanistic rather than empirical models are to be developed. Accordingly, there is a need to explicitly address the topic of process coupling both experimentally and computationally. While many subsurface systems may be adequately simulated using combinations of isolated processes (linear combinations), the actual macroscopic system behavior may not be well represented. Examples include differences between biological or chemical reaction rates measured under laboratory conditions generally exceeding actual rates in the field, or changes in biogeochemical process rates that both depend on, and also modify, mass transport in porous media. Discrepancies between predictions and field observations, for example, are often explained by parameterization errors—resolved by using additional adjustable or effective parameters. Conceptual models that do not account for process coupling may incorrectly predict contaminant fate and transport in systems deviating from those in which models were originally developed. In particular, in systems undergoing rapid (non-equilibrium) change, which is typical for many remediation activities, the importance of addressing process coupling will be magnified. In addition, the data from such systems is typically distributed in both space and time, so a coupled conceptual/numerical model is required to interpret these. Therefore, experimental research and model development needs to be directed at resolving and parameterizing coupled processes (in particular reaction kinetic and mass transfer rates) and imparting this information within comprehensive computational models.